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PICOGRAM FT-IR: ULTRAMICROSAMPLING AND GC-IR

Tomas Hirschfeld

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Picogram Fourier transform-Infrared (FT-IR):  
Ultramicrosampling and gas chromatograph-infrared (GC-IR)\*

Tomas Hirschfeld  
Chemistry & Materials Science Department, Lawrence Livermore National Laboratory  
P. O. Box 808, L-322, Livermore, California 94550

Abstract

The commonality between ultramicrosampling and GC-IR is far deeper than the desire for picogram detection levels in both cases. Both techniques also need small area light spots: in ultramicrosampling, for spatial resolution; and in GC-IR, to match limited sample volumes. Fast response is needed for real-time measurements on the fly GC-IR, and for mapping analysis of extended samples in a finite line in ultramicrosampling. And finally, the fly fast processing is required for real-time recognition of significant success in GC-IR (presence of peaks) and in ultramicrosampling (presence of local anomalies in sample).

A small FT-IR interferometer benefiting from the counter-Jacquinot advantage (and some less awkward nomenclature is clearly required here), immersion optics for microsampling and optimized sample cells for GC-IR, high efficiency sources and detectors (and detector electronics!), and the systematic application of information theory to data processing algorithms can be used to bring both these techniques into the middle picogram domain. Progress from here will require cryogenic sampling GC-IR (giving only small improvements over an optimized light pipe) or non FT-IR techniques, such as grating (shudder!) scanned CO<sub>2</sub> lasers (capable of a >100 fold gain).

The ultramicro analysis capability of fourier transform spectroscopy is a sheep in wolf's clothing. It is undoubtedly true that the FT-IR can get you good infrared spectra of 25-micron diameter samples, or even smaller ones. It is much less true that it can accomplish this in any practical fashion for the average infrared sample.

The problem is that there is no reliable way of recognizing, by other than infrared spectroscopy means, which portion of the sample one should be looking at. If the region of the sample that is different in the

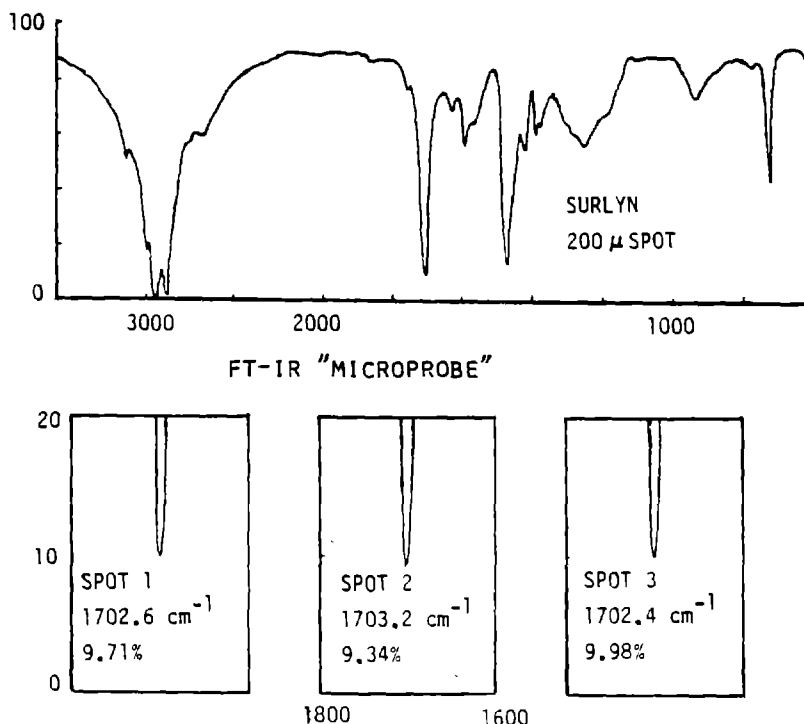


Figure 1. Infrared microprobe scan of Surlyn film.

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infrared is immediately recognizable (from observations with a light microscope, for example), then the ability to measure a small point and get its infrared spectrum is all that is desired. However, if the sample that is abnormal in the infrared is not distinguishable by some other means of observation, then what we need is not infrared ultramicrosampling, but, instead, infrared microprobing. Here a microsampled spot can be scanned over the surface so that we measure the infrared properties not at one point, but at thousands of points over the surface, until we find the one that is of interest (Fig. 1). Unfortunately, this defines a requirement for measuring in a reasonable time, not just point's spectrum, but many thousands of those. This clearly requires a quantum jump in the state-of-the-art of sampling microspots on the surface. Not only must we sample a great many points, but we must sample them at a high speed with a continuously mechanically scanned sample. We must store excessive amounts of data, and we must process it equally fast.

The first element of obtaining a powerful microprobe capacity in an FT-IR system is to increase sampling speed by using optical immersion around the sample. In those instances where this is feasible, such as pliable thin film samples, the use of a curved window in contact with the sample decreases the size of the infrared beam at the beam waist and enables one to get a much larger transmission through a small sample spot. In such a way, a pair of germanium hemispheres scanned over a plastic film can give much better spot resolutions or get much higher energy throughputs and measurement speed through a given spot size. This technology can also be applied as window caps to the diamond cell used in high pressure FT-IR.

Another thing that we can do when we go to these very small systems is to reduce the detector size, which need not be larger than the size of the sample. These smaller detectors have far less noise. This is, of course, at considerable variance with what we normally think of as the throughput advantage of FT-IR. For small samples, such as encountered in infrared microprobe, this throughput advantage is illusory. As our sample gets smaller, the throughput required of the instrument gets smaller, the size required to intercept all of the available beam is less, and the smaller, lower noise detector now has a net advantage.

In such a very small detector, an immersion lens should be used to further reduce the size of the detector needed to intercept a given beam. The detector is mounted in a miniature microrefrigerator and illuminated by on-axis concentrating optics (which have much lower aberrations). In this way, we are able to use a 50 $\mu$ -diameter mercury cadmium telluride detector whose immersion lens gives it the light-gathering power of a 125-micron diameter one. The miniature refrigerator allows operation of the detector without the need for liquid nitrogen (Fig. 2).

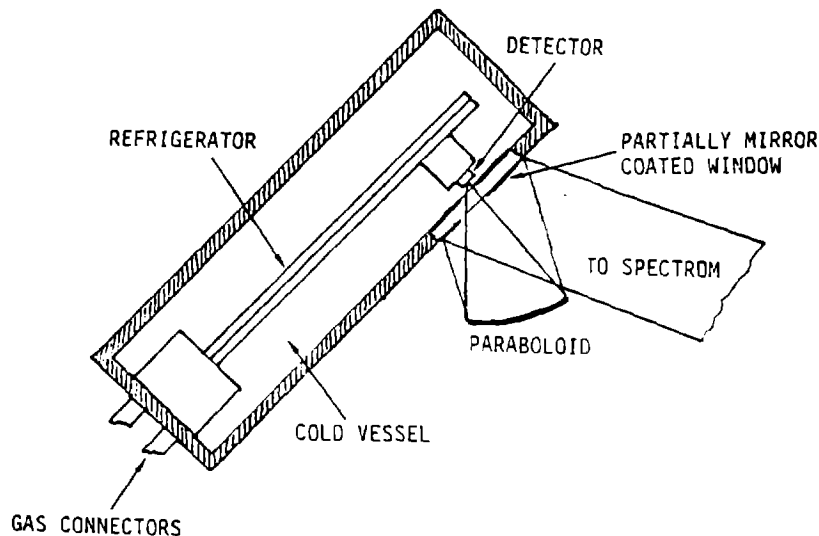


Figure 2. Microminiature cryogenic detector assembly.

In measurements on such very small samples, problems were encountered with spectral distortion produced by interference phenomena in very small pinholes. These distortions, however, were mainly due to the thickness of the pinhole. For a small diameter pinhole in a thick plate, distortion will be produced by waveguide effects. The problem can be avoided by forming the pinhole in a thin plate.

The technology of using very small detectors, and of using immersion wherever possible, has been applied to the measurement of the spectra of very small samples of a high explosive used in detonators. Despite the 50 $\mu$  sample diameter, there is enough signal to noise to measure the difference spectra produced by heat treatment of the sample (Fig. 3). We can also see spatial fluctuations in the sample at this size scale (Fig. 4).

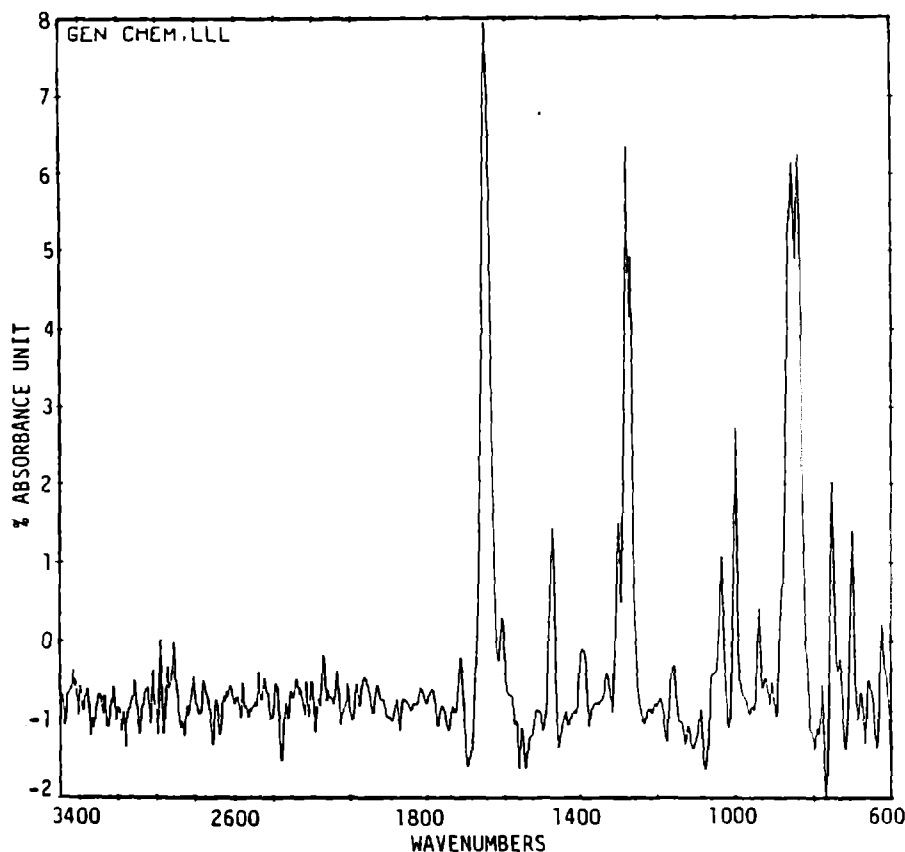
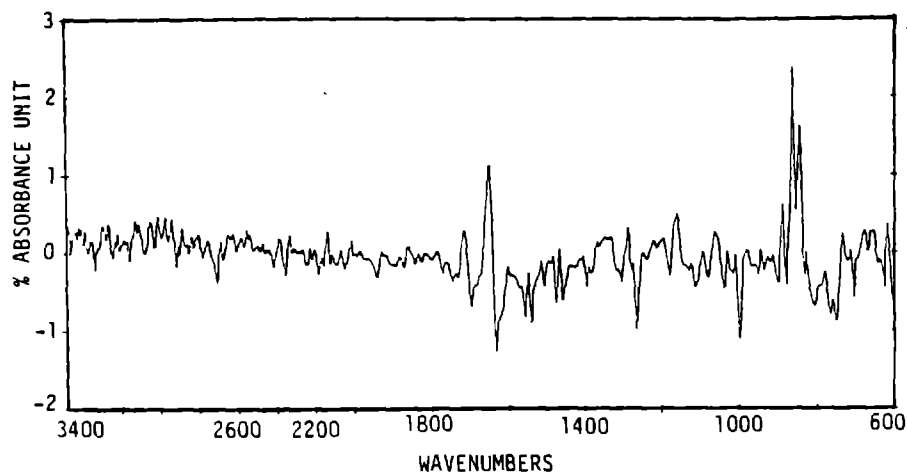


Figure 3. Absorbance subtract measurement of heating effects in an explosive measured at 50  $\mu$  spatial resolution.

Figure 4. Absorbance subtract measurement of local variability in an explosive measured for a 50  $\mu$  (using bulk measurements as a reference).



Much else can be done in improving the hardware used for ultramicrosampling FT-IR, particularly when we want to use it as a microprobe. This includes using the brightest source we can get (a high-temperature blackbody), conserving the light through the system (high efficiency beam splitters, high aperture optics), avoidance of off-axis optics, and even, when possible, using multiple detectors to gain signal to noise ratio and operating speed.

In addition to that, we also need to improve the system software. The task here is to do rapid scanning of a very large number of sample points, a few of which have relevant information. The similitude of this to GC-IR is quite evident. We can thus use Gram-Schmidt controlled scanning where a scanning microscope stage

scans through a large number of points, and interferogram's Gram-Schmidt function is used to stop the scan at appropriate points for more detailed observation. Here, we can also use second derivative data. Of course, using an array of detectors to scan several points simultaneously calls for a very large change in software.

In general, there are many opportunities for using software adapted from GC-IR technology in ultramicro-sampling. Here we must consider the isolation of significant scans so that we don't have to store all the data, and hopefully avoid even measuring it, as described above. Furthermore, we can use the same algorithm as used in GC-IR to find out whether contiguous spots can be averaged together. Here, the use of sequential absorbance ratios is, of course, quite important. We can also think of data cleanup procedures like machine resolution of partially overlapped peaks, quantitation procedures of GC-IR like selective co-adding of peaks, and weighted averaging. And, finally, we can use some of the data display techniques of GC-IR including isometric displays, contour displays, significance plots, confidence spectra, etc.

In addition to these things, infrared microprobing can use some sample preparation tricks, like exposing samples to iodine vapors to give surface markings indicating the distributions of organics on a surface. This is particularly useful when small traces of organic contaminants have to be located on a largely inorganic surface where iodine will color the organic brown spots without greatly altering the spectrum (Fig. 5).

Some examples of the power of such improved techniques are not in order. These include ultramicro FT-IR measurement of particles precipitated on a gasket (Fig. 6), and another spectra of lubricant contamination particles (Fig. 7). The interesting point about each of these spectra is that they were obtained very rapidly with one or just a few scans, and, thus, in a mode compatible with microprobe operation. The operation of FT-IR as a microprobe, with a 25-micron pinhole, can be seen in a scan of the content of wax in HMX explosive (Fig. 8). We can see that the wax is concentrated on the grain boundaries of the material.

Much more needs to be done before FT-IR microsampling becomes practical high speed FT-IR microprobing, a transition that will be necessary before this technique can be used widely on the average sample.

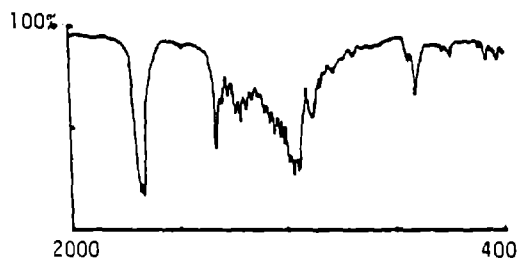


Figure 5. Spectrum of a 35  $\mu$  lubricant particle in HMX explosive after marking with iodine vapor.

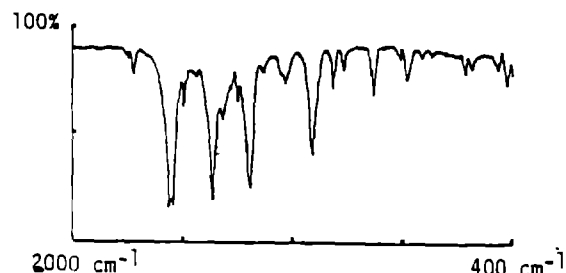


Figure 6. Spectrum of a 21  $\mu$  particle precipitated on a rubber gasket.

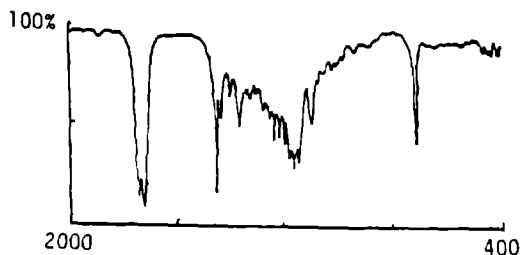


Figure 7. Spectrum of a 12  $\mu$  lubricant particle on HMX explosive.

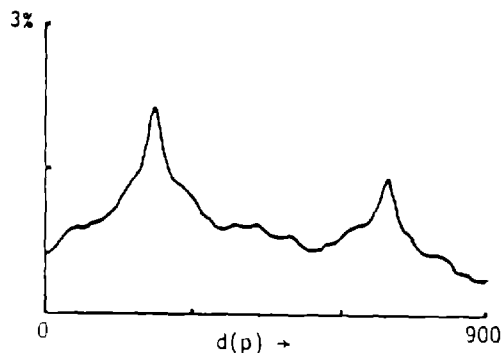


Figure 8. FT-IR microprobe scan of wax content in HMX explosive, measured at 25  $\mu$  resolution.